Effect of hydrogen-related impurities on the thermal behavior of mechanical stress in silicon oxides suitable for integrated optics

C. Domínguez[a)]
Instituto de Microelectrónica de Barcelona (IMB-CNM, CSIC), Bellaterra 08193, Barcelona, Spain

J. A. Rodríguez[b)]
Physics Faculty, Havana University, San Lázaro y L, 10400 Vedado, Havana, Cuba

M. Riera and A. Llobera
Instituto de Microelectrónica de Barcelona (IMB-CNM, CSIC), Bellaterra 08193, Barcelona, Spain

B. Díaz
Phys. Fac., Havana University, San Lázaro y L, 10400 Vedado, Havana, Cuba

Silicon oxide films were deposited by plasma enhanced chemical vapor deposition on crystalline silicon substrates from a mixture of silane and nitrous oxide. Substrate temperature and $[N_2O]/[SiH_4]$ precursor gas flow ratio were varied between 200–350 °C and 5.5–110, respectively. Rapid thermal annealing at 900 °C to achieve impurity effusion led to significant changes in the dependence of the mechanical stress with the gas flow ratio R. *In situ* stress measurements during thermal cycles up to 300 °C as well as measurements of transmission infrared spectra for the as-deposited and annealed samples were performed. The changes in the stress behavior were explained considering the layer shrinkage resulting from the effusion of the different impurities present and the network rearrangement taking place during rapid thermal annealing, for different ranges of flow ratios. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1563297]

I. INTRODUCTION

Increasing interest is currently devoted to silicon-rich silicon oxides (SiO_X, $X<2$) deposited at low temperature by plasma enhanced chemical vapor deposition (PECVD) with silane (SiH_4) and nitrous oxide (N_2O) as precursor gases. Silicon suboxides (as they are also called) have been widely used as intermetal dielectric layers, positively impacting the microelectronic industry.[1,2] Furthermore, they are being effectively employed as basic materials for passive elements in integrated optics technology[3,4] as well as for fundamental studies about the luminescent properties of silicon-based nanostructures and silicon oxide defect centers.[5,6] The composition and physical properties of these materials strongly depend on the deposition parameters, particularly, the precursor gas flow ratio R (defined as $R=[N_2O]/[SiH_4]$) and the substrate temperature T_s.[7] During deposition, impurities such as hydrogen, nitrogen, and water are introduced within the layers. Moreover, moisture is generally incorporated from the atmosphere after deposition. As a result, Si–H, Si–OH, Si–N, H–O–H, and N–H bonds are present, in addition to Si–O bonds, influencing the properties of the films. When used as integrated optic materials, impurity bonds enhance optical absorption, increasing transmission losses. Thermal processing to achieve film impurity effusion often causes structural changes giving rise to different stress-related phenomena affecting the film/device integrity

and behavior. These facts suggest the importance of controlling stress values in film-substrate structures as a function of deposition parameters.

Rapid thermal annealing (RTA) at 900 °C is an effective way to achieve impurity effusion.[8] The short process duration (around 30 s) avoids the occurrence of other undesirable physical and chemical processes, such as diffusion and oxidation. In a previous work,[8] we reported the effect of RTA on the mechanical stress of PECVD silicon oxide films deposited on silicon wafers at 300 °C with different gas flow ratios. We showed (through Fourier-transform infrared, FTIR, measurements) that a complementary effect exists for the as-deposited films: films deposited with low gas flow ratios are Si-rich with high concentrations of Si–H bonds, while films deposited with high R-values are more stoichiometric, with lower Si–H bond content. Thus, changes in stress with RTA in samples deposited with small R values (R less than about 15) were explained on the basis of the film shrinkage due to effusion of hydrogen from the Si–H bonds. For higher R values, where the Si–H bond concentration is below the detection limit of the FTIR technique, the changes in stress remained unexplained.

To definitively clarify the stress behavior after RTA, we report in the present article a full study of the effect of the different H-related impurities in the stress of PECVD silicon oxide layers deposited with different T_s and R values and subjected to several thermal treatments. During the rapid thermal annealing at 900 °C the effusion of all the impurities takes place simultaneously, being impossible to discriminate the particular effect of each one. Therefore, we analyze here the results obtained by subjecting the oxide films to thermal

[a)]Author to whom all correspondence should be addressed; electronic mail: carlos@cnm.es
[b)]Electronic mail: jar@ff.oc.uh.cu

5125

cycles up to 300 °C, with simultaneous stress measurements. The layer composition of the as-deposited samples and after each thermal treatment is qualitatively studied by Fourier-transform infrared spectroscopy (FTIR). Somewhat similar analyses may be found in the literature for a fixed value of flow ratio.[9] However, the effect of impurities on stress as well as on other physical properties strongly depends on the type and concentration of these impurities, which in turn, depend on R.

II. EXPERIMENT

The deposition processes were achieved on a large radial flow capacitively coupled parallel-plate PECVD reactor, operated at 13.56 MHz. Details of the installation can be found elsewhere.[10] Undiluted silane and nitrous oxide were used as precursors. Chamber pressure, r.f. power density, and nitrous oxide flow during depositions were fixed at 26.6 Pa, 0.07 W/cm^2, and 110 sccm, respectively. The $[N_2O]/[SiH_4]$ flow ratio and the substrate temperature were varied in the ranges 5.5–110 and 200–350 °C, respectively. The films were deposited on one-side polished p-type (14–20 Ohm-cm) silicon (100) wafers (50 mm in diameter and 240 μm as average thickness). Layers of thickness about 1.0 μm, similar to those used for integrated optics applications, were obtained. Thickness values were measured with a Rudolph Research Auto El IV ellipsometer operated at 632.8 nm and 70° incidence angle. Stress was determined by measuring the substrate strain (change in curvature) induced by the deposited layer. The wafer curvatures were found with an optically levered laser technique. *In situ* measurements of the stress variations during thermal cycles were carried out placing the samples in a furnace with a window for the laser beam. The heating rate was 20 °C/min, approximately. The rapid thermal annealing was achieved in an ADAX-1000 system, at 900 °C, on inert atmosphere. The mean heating rate was 32 °C/s and the annealing time was 30 s. In both cases, cooling was done by switching off the power. Transmission FTIR spectra were obtained with a Perkin-Elmer Model 2000 spectrophotometer, the reference being a silicon wafer analogous to the substrates.

III. RESULTS AND DISCUSSION

Figure 1 shows the total stress as a function of flow ratio. The same features found in Ref. 8 appear again. We have repeated the corresponding measurements since a new reactor has been employed and a wider range of R is analyzed. Two curves of stress are presented in Fig. 1: one belonging to the as-deposited samples (straight curve) and the second obtained after RTA (broken curve), the deposition temperature being 300 °C. The broken curve determines two well-defined regions, referred hereafter as low-R and high-R regions.

It is a well-known fact that the value of the total stress is proportional to the curvature of the film-substrate structure, which is produced during the deposition process and cooling down to room temperature. The curvature is considered to be negative (compressive stress) in convex structures when observed from the oxide side, and positive (tensile stress) in concave structures. As observed in Fig. 1, as-deposited
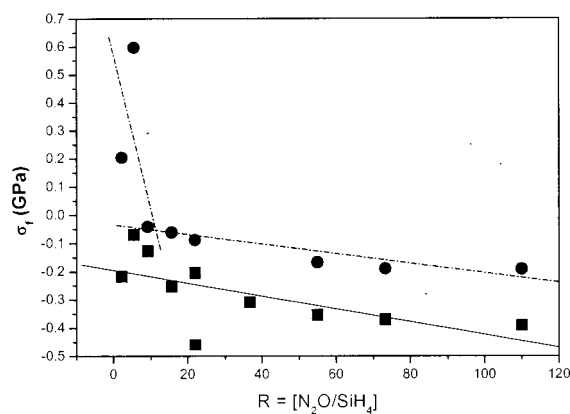

FIG. 1. Total mechanical stress as a function of gas flow ratio (R), before (straight line) and after (broken line) RTA.

PECVD silicon oxide films deposited on crystalline silicon wafers are under compressive stress, i.e., convex structures are obtained. For annealed samples, stress is less compressive than for the as-deposited ones (structures become less convex or even concave after RTA), both in the low-R and high-R regions. This fact should be associated to film shrinkage during RTA. However, as it will be demonstrated below, the causes of this shrinkage are somewhat different for the two regions.

Table I shows the evolution of the FTIR bands for samples deposited at 300 °C with R ranging from 5 to 110. Figure 2 illustrates the corresponding spectra for representative samples. For comparison, a spectrum of thermal oxide is also inserted. Previous to the infrared measurements, the samples were kept in controlled atmosphere with 85% relative humidity for a week to allow for moisture incorporation. The evolution of the impurity-related bands is clearly shown. All these bands disappear during RTA (spectra are not shown for simplicity). Some important remarks can be made.

(1) The three fundamental Si–O vibration bands (rocking, bending, and stretching) are present in all spectra except for $R=5$, where the bending peak is not resolved.

(2) The Si–O stretching peak, in 1040 cm^{-1} for $R=5$, shifts to higher wave numbers for increasing R, being located at around 1080 cm^{-1} for spectra corresponding to $R=22$. Moreover, these spectra markedly resemble that of thermal oxide, indicating a stoichiometric silicon oxide.

(3) A systematic evolution of the spectra from 750 to 900 cm^{-1} for R between 5 and 11 is observed. For $R=5$, an important band at 870 cm^{-1} is present. As R increases, this band shifts to higher wave numbers (882 cm^{-1} for $R=11$) and its intensity decreases. This band is probably associated to the Si–H bond bending mode in the H–Si–O$_3$ configuration.[1,11] In fact, the intensity of this band is directly related to the one at 2240 cm^{-1} which has been associated with the stretching of Si–H when back bonded to three oxygen atoms.[1] Both bands practically vanish for $R>11$. Simultaneously, the intensity of the Si–O bond bending band at around 810 cm^{-1} increases for increasing R. This fact, jointly with remark (2) indicates an increasing level of oxidation.[1,12,13]

TABLE I. Wave number (cm^{-1}) of the different absorption FTIR bands as a function of gas flow ratio (R).

	Wave number (cm^{-1})								
R	Si–H (b)[a]	Si–H (s)[b]	N–H (s)[b]	Si–O (r)[c]	Si–O (b)[a]	Si–O (s)[b]	H–O–H (s)[b]	Si–OH (b)[a]	Si–OH (s)[b]
5.00	870	2240	3378	430	—	1040	—	—	—
8.46	884	2266	3390	452	812	1048	—	—	—
9.17	884	2272	3390	452	812	1050	—	—	—
11.00	882	2272	3382	452	816	1066	—	—	—
22.00	—	—	—	452	808	1080	1620	938	3658
36.70	—	—	—	452	816	1080	1612	(938)	3660
55.00	—	—	—	452	818	1076	1612	(938)	3660
110.00	—	—	—	452	818	1080	1600	(938)	3660

[a](b) bending.
[b](s) stretching.
[c](r) rocking.

(4) No bands associated with Si–OH or H–O–H bonds are observed for the smaller R values, in agreement with the moisture blocking mechanism inherent to Si–H bonds proposed by Machida *et al.* (an almost undetectable stair is observed for $R=11$ at around 3660 cm^{-1}).[14] Instead, a band is observed at around 3380 cm^{-1} associated with N–H bonds stretching[1]. This band correlates with the Si–H bands mentioned before; its intensity decreases with increasing R.

(5) Three different moisture-related bands are observed in the FTIR spectra of samples corresponding to the high-R region (R in the range 22–110, in Fig. 2): the first one is a small band at around 1620 cm^{-1} assigned to H–O–H bonds[15] (molecular trapped water). The second is a wide band in the range 3300–3700 cm^{-1} formed by a broad band and a stair at around 3660 cm^{-1}, associated with the Si–OH stretching.[16,17] The third is a small band at around 930 cm^{-1}, due to the Si–OH bending vibration.[16,17] All moisture-related bands have maximum intensity for the $R=22$ sample, gradually decreasing toward higher and smaller R values, and disappearing in the samples with a higher concentration of Si–H bonds.

In summary, the evolution of the spectra between 750 and 1100 cm^{-1} indicates that as R increases, the oxide films become more stoichiometric. The concentration of Si–H and N–H bonds increases as R decreases, while the concentration
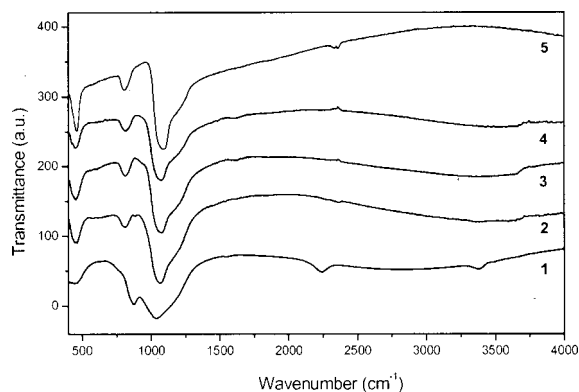
of OH and H$_2$O peaks at $R=22$ approximately. Most of these changes can be understood considering the chemical reaction taking place during the deposition process. Basically, as R increases, the concentration of O species activated by electron impact dissociation also increases. Then, the Si atoms tend to be efficiently passivated by the strongly electronegative oxygen atoms and Si–H bonds are inhibited (the energy of the Si–O and Si–H bonds are 8.4 and 3.0 eV, respectively[18]). The presence of Si–H bonds in samples deposited with smaller R inhibits that of Si–OH and H–O–H, the concentration of which grows up to $R=22$ (stoichiometric sample) and then decreases, probably due to the lessening of porosity for R between 22 and 110.

In the light of the above observations, it is now possible to analyze the behavior of the stress with R, before and after the RTA (Fig. 1).

A. Analysis of low-R region

After RTA, the stress of the samples in the low-R region increases abruptly as R decreases (Fig. 1). It is due to film shrinkage resulting from the impurity effusion (breaking of Si–H and N–H bonds) during the annealing. Si–H and N–H bonds concentration increases for smaller R (remark 3), so the shrinkage and the stress increase should be greater as well, as experimentally observed.

To analyze the relative strength of H-related bonds in the low-R range, we studied the evolution of the film stress as a function of temperature, subjecting the layers to thermal cycles up to 300 °C. Figure 3 displays the corresponding curves for a sample with an extreme R value (5.5). No appreciable difference is observed in the stress values on cooling relative to those obtained on heating. Therefore, annealing up to 300 °C does not generate the effusion of impurities, probably due to the local environment H–Si–O$_3$. In this case, the silicon atom is back bonded to three oxygen atoms (strongly electronegative) and consequently the H–Si bond strength is important. To verify qualitatively this assertion, a sample obtained with the same deposition parameters was subjected to successive thermal treatments with increasing temperatures, and the corresponding infrared spectra were measured (Fig. 4). Annealing at 600 °C was necessary to detect a significant reduction of Si–H and N–H bands. They

FIG. 2. FTIR spectra corresponding to some of the samples deposited at 300 °C at different gas flow ratio (R) values. (1) $R=5$, (2) $R=11$, (3) $R=36.6$, (4) $R=110$, and (5) thermal oxide.
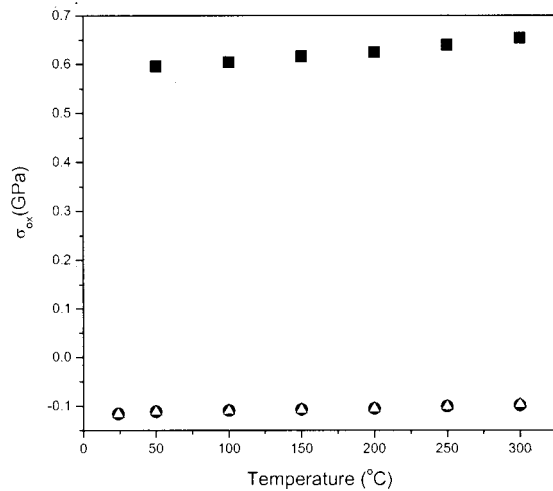
FIG. 3. Evolution of total mechanical stress with temperature for a sample deposited at 300 °C and $R=5.5$. (●) First cycle heating, (△) first cycle cooling, and (■) after RTA.

FIG. 5. Evolution of total mechanical stress with temperature for a sample deposited at 300 °C and $R=22$. (●) First annealing cycle, (■) after RTA.

completely disappeared during RTA at 900 °C (Fig. 4), as stated above.

The sample subjected to a thermal cycle up to 300 °C was next annealed by RTA at 900 °C, to reach the next impurity effusion step. A new thermal cycle up to 300° was then accomplished. The corresponding stress-temperature dependence is shown in Fig. 3. A drastic inversion of the film curvature, from convex to concave, is observed (the stress changed from negative to positive), in accordance with H-related impurity effusion and the corresponding pronounced film shrinkage.

B. Analysis of high-R region

The differences in the stress values before and after RTA in the high-R region are significantly lower than in the preceding case. Important impurity bands related to Si–OH and H–O–H bonds are, however, present in this region. The effusion of these impurities should also produce a significant film shrinkage, but this was not the case. To clarify this apparent contradiction, a sample with $R=22$ [stoichiometric oxide according to remark 2 and maximum intensity of the

Si–OH related bands (remark 5)] was subjected to the thermal cycle up to 300 °C. Figure 5 shows the corresponding curves for the heating and the cooling processes. On heating above 100 °C the stress increases, i.e., the film contracts and the structure curvature decreases. On cooling, a linear (elastic) behavior is observed and an important stress hysteresis in the full cycle is obtained. Figure 6 depicts a study by transmission infrared spectroscopy (FTIR) of a sample deposited under similar deposition parameters. Spectra were measured just after deposition, after exposure to free atmosphere for two months and after thermal treatments at different temperatures during 30 min. Just after deposition, the small band at about 930 cm^{-1}, as well as the low wave-number side of the broad band at around 3300–3700 cm^{-1}, associated to Si–OH bending and stretching, respectively, are missing. Only the high wave-number side of the last band, i.e., the stair at around 3660 cm^{-1}, is present. However, the absent bands appear after the stay in free atmosphere. Moreover,
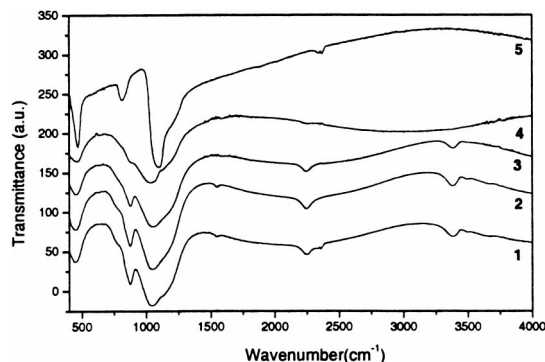

FIG. 4. FTIR spectra for a sample deposited at 300 °C and $R=5.5$, after thermal (30 min) and RTA (30 s) annealing at different temperatures. (1) As-deposited, and (2) annealing at 400 °C, (3) annealing at 600 °C, (4) RTA annealing at 900 °C, and (5) thermal oxide.
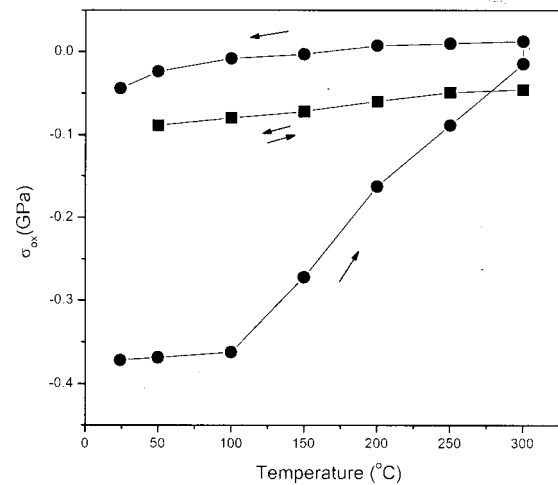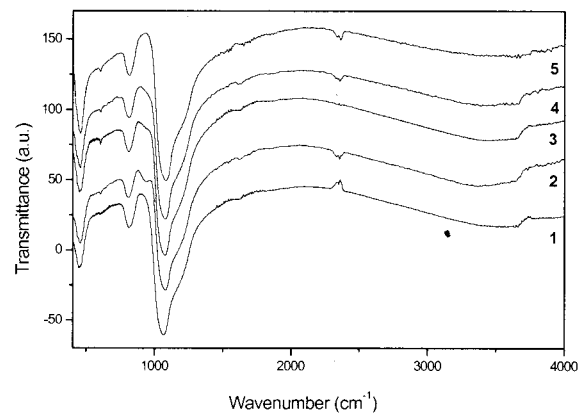

FIG. 6. FTIR spectra for a sample deposited at 300 °C and $R=22$ after thermal annealing during 30 min at different temperatures. (1) As-deposited, (2) after six months exposed to room atmosphere conditions, (3) after annealing at 300 °C, (4) after annealing at 400 °C, and (5) after annealing at 500 °C.

thermal annealing at 300 °C eliminates all Si–OH related bands but the stair, which requires 500 °C annealing to be eliminated.

The observed behavior of Si–OH related bands can be satisfactorily explained in the light of the model proposed by Theil *et al.*[17] and used by Haque, Naseem, and Brown.[9] In this model, three main local environments are proposed for silanol (Si–OH) group in PECVD silicon oxides: near-neighbor, partially shielded and completely isolated (by silicon oxide matrix) Si–OH groups. According to these authors, the mentioned environments lead to a broad absorption band in the range 3300–3700 cm^{-1} and a little band at about 930 cm^{-1}, in agreement with our experimental results. The first environment is responsible for the lower wave-number side of the broad band as well as for the band at 930 cm^{-1}. It is produced by the incorporation of moisture during the post-deposition stay of the films in room atmosphere and results from the attack of strained Si–O–Si groups (commonly encountered in PECVD silicon oxide) by water molecules. In our case, a shift of the Si–O bond stretching band from 1069 to 1080 cm^{-1} was observed during ageing, in correspondence with the fact that water vapor reacts preferentially with the more reactive groups with lower Si–O–Si angles[17] [the typical value of this angle for relaxed material is about 144° (Ref. 19)] responsible for the absorption in the lower frequency side. On the contrary, isolated silanol groups contribute to the higher wave-number side of the broad band (the little stair observed in the spectra of Fig. 6) and are formed during deposition and/or cooling down of the sample in the deposition chamber. The isolated character of these bonds should correspond to a higher effusion temperature, a fact observed in our experiments.

In summary, the trend observed in Fig. 5 under the thermal cycle up to 300 °C should be due to the release of near-neighbor Si–OH groups, that are formed during ageing due to moisture incorporation into the oxide. On heating, moisture effuses and the film contracts, thus producing the corresponding stress hysteresis.

Figure 5 also shows the stress-temperature curve measured after a subsequent RTA at 900 °C. Even though the RTA produces the release of the remaining moisture (completely isolated Si–OH bonds) with an additional shrinkage, the curve shifts down, indicating a film expansion. This might be due to stress relief, and a corresponding increase of the Si–O–Si bond angle at the bridging oxygen atom site, as a consequence of the reordering of the oxide network during the annealing in this almost stoichiometric oxide film. This hypothesis is supported by a slight shift of the Si–O stretching band to higher wave numbers. Therefore, for the corresponding R value, the film contraction associated to rapid thermal annealing due to impurity effusion is partially compensated by a film expansion due to stress relief. The combination of these two effects explains the low stress differences before and after RTA in the high-R region.

C. Effect of substrate temperature

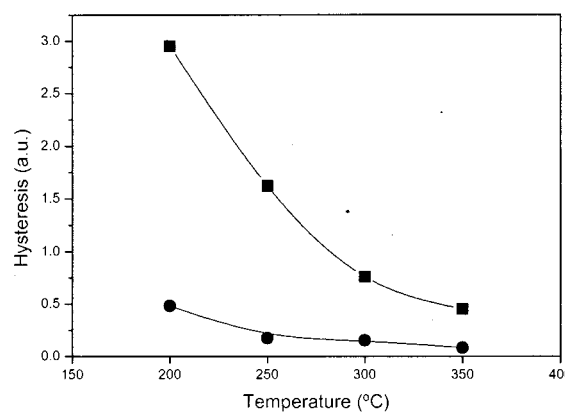All the particularities analyzed in the preceding paragraphs are present in PECVD silicon oxide irrespective of

FIG. 7. Stress hysteresis as a function of deposition temperature for samples deposited at (●) $R = 5.5$ and (■) $R = 20.7$.

the substrate temperature. For lower values of this parameter, however, the effects associated to Si–OH bonds should be more pronounced. To verify this assertion, a set of films was deposited under the same deposition conditions, with two extreme R values (20.7 and 5.5) and four different substrate temperatures (200, 250, 300, and 350 °C). After exposure to free atmosphere, thermal cycles up to 300 °C, followed by RTA, were carried out. Similar features to those shown on Figs. 3 and 5 (according to R) were obtained. In order to analyze the results, a magnitude called "hysteresis" is defined as the difference, at a fixed temperature of 50 °C, of the stress values during cooling and heating processes. For $R = 5.5$ the hysteresis is very little even for samples deposited at 200 °C, presumably due to the absence of moisture because of the blocking mechanism of Si–H bonds (see Fig. 7). For $R = 20.7$, hysteresis is always higher than for $R = 5.5$. Furthermore, it increases for smaller substrate temperatures. This behavior is in agreement with higher moisture contents for samples deposited at lower temperatures, as expected from more porous oxides.

IV. CONCLUSIONS

The effect of the different thermal processing on mechanical stress in PECVD silicon oxide films deposited on c-Si substrates depends to a great extent on the reactant flow ratio and substrate temperature. This dependence takes place through the type and concentration of H-related impurities, mainly in the form of Si–H, N–H, H–O–H, and Si–OH bonds. During RTA at elevated temperature, film shrinkage is observed as a result of impurity effusion and oxide network rearrangement. For low R values (lower than about 15), a high concentration of Si–H bonds is present, incorporation of moisture is blocked, and the effusion of impurities during annealing leads to a high film contraction with a significant stress variation. For high R values (higher than about 15) the concentration of Si–H is low and moisture is present as H–O–H and Si–OH bonds in different local environments. During annealing, two simultaneous mechanisms take place, impurity release and bonding relief, which partially compensate for one another, and the resulting net film shrinkage as well as the film stress variations are low.

ACKNOWLEDGMENTS

[1] A. Sassella, A. Borghesi, F. Corni, A. Monelli, G. Ottaviani, R. Tonini, B. Pivac, M. Bacchetta, and L. Zanotti, J. Vac. Sci. Technol. A **15**, 377 (1997).

[2] C. F. Lin, W. T. Tseng, and M. S. Feng, J. Appl. Phys. **87**, 2808 (2000).

[3] H. S. Han, S. Y. Seo, J. H. Shin, and D. S. Kim, J. Appl. Phys. **88**, 2160 (2000).

[4] I. Garcés, F. Villuendas, J. Subías, J. Alonso, M. Del Valle, C. Domínguez, and E. Bartolomé, Opt. Lett. **23**, 225 (1998).

[5] Z. Ma, X. Liao, J. He, W. Cheng, G. Yue, Y. Wang, and G. Kong, J. Appl. Phys. **83**, 7934 (1998).

[6] S. Y. Seo and J. H. Shin, Appl. Phys. Lett. **25**, 4070 (1999).

[7] H. J. Schiliwinski, U. Schnakenberg, W. Kindbracke, H. Neff, and P. Lange, J. Electrochem. Soc. **139**, 1730 (1992).

[8] C. Domínguez, J. A. Rodrguez, F. J. Muñoz, and N. Zine, Thin Solid Films **346**, 202 (1999).

[9] M. S. Haque, H. A. Naseem, and W. D. Brown, J. Appl. Phys. **82**, 2922 (1997).

[10] C. Domínguez, J. A. Rodríguez, F. J. Muñoz, and N. Zine, Vacuum **52**, 395 (1999).

[11] D. V. Tsu, G. Lukovski, and B. N. Davidson, Phys. Rev. B **40**, 1795 (1989).

[12] P. G. Pai, S. S. Chao, and T. Takagi, J. Vac. Sci. Technol. A **4**, 689 (1986).

[13] C. Falcony, W. Callejas, M. Aceves, J. M. Siqueiros, R. Chamorro, L. Cota-Araiza, G. Soto, and M. H. Farías, J. Electrochem. Soc. **144**, 379 (1997).

[14] K. Machida, N. Shimoyama, J. Takahashi, Y. Takahashi, N. Yabumoto, and E. Arai, IEEE Trans. Electron Devices **41**, 709 (1994).

[15] R. Etamadi, C. Godet, J. Perrin, J. E. Bourée, B. Drévillon, and C. Clerc, Surf. Coat. Technol. **80**, 8 (1996).

[16] A. C. Adams, F. B. Alexander, C. D. Capio, and T. E. Smith, J. Electrochem. Soc. **7**, 1545 (1981).

[17] J. A. Theil, D. V. Tsu, M. W. Watkins, S. S. Kim, and G. Lukovsky, J. Vac. Sci. Technol. A **8**, 1374 (1990).

[18] M. Zacharías, T. Druzeau, A. Panckow, H. Freistedt, and B. Garke, J. Non-Cryst. Solids **169**, 29 (1994).

[19] A. G. Revesz, J. Electrochem. Soc. **146**, 2225 (1999).